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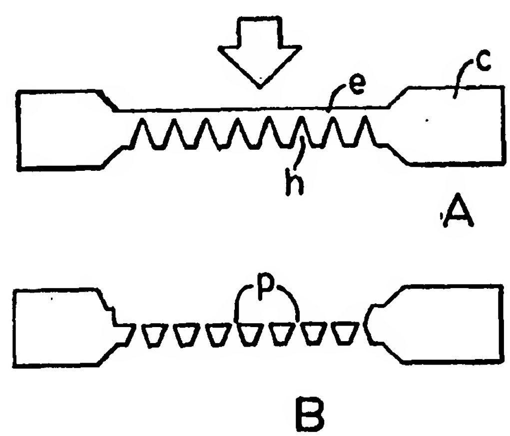
(54) Title: *IN SITU* MANUFACTURE OF MEMBRANE MICROFILTERS

(57) Abstract

Membrane microfilters are formed *in situ* in a defined region of a blank (c) by embossing one surface of the defined region (e) of the blank (c) to provide an array of indentations (h), and ablating the material of the blank in the defined region until the indentations become through pores (p). Ablation may be carried out by various means such as chemical etching or laser ablation.



IN SITU MANUFACTURE OF MEMBRANE MICROFILTERS

This invention relates to the manufacture of membrane microfilters.

Membrane microfilters, as opposed to depth filters, function as simple sieves. If a fluid suspension is passed through a membrane microfilter, all objects within that suspension under a certain size (the pore size) are permitted to pass. Everything else is held back and captured on the membrane microfilter's surface. The quality and performance of membrane microfilters are characterized by the pore size distribution, the number of pores in a given area (porosity), and the degree of overlap between pores (doublets and triplets, etc.).

The dominant technology for the production of membrane microfilters (that is, with pore sizes in the micron range) is the track-etch technique. In this technique, a thin polymeric film is exposed to a collimated beam of massive, energetic nuclei such as U^{235} fission fragments. As the nuclei pass through the film, they break the polymer's backbone bonds, leaving a directed trail of defects. In a second and final step, the film is placed in a warm caustic bath where the defect trails are preferentially etched against the bulk of the material. The result is a set of microscopic pores whose average size can be controlled by the etch parameters (temperature, concentration, time) and whose surface density is controlled by the length of time the film is left in the particle beam.

There are several problems associated with the manufacture, quality, and application of conventional track-etched membrane microfilters.

The use of the track-etch technique places numerous restrictions on the materials used, their thickness and composition. They cannot be too thick or the fission fragments will not leave a complete defect trail. Nor can they be conductive or the charge build-up will distort the otherwise collimated beam. The technique is rather difficult to apply in practice, requiring as it does a particle beam source, which may represent a considerable investment. The

track-etching takes place under restrictive conditions that make it impractical to process anything other than continuous rolls of polymeric film material. The second stage etching process is difficult (though not impossible) to control and any piece produced in this way must be further processed to remove traces of the harsh chemical used to manufacture the part.

The point of collision between the individual particles and the polymeric film cannot, in general, be controlled. As a consequence, the distribution of the defect trails over the surface of the polymer film is random. One consequence is that the arrangement of pores is also random. Another is that there is a high probability of pore overlap if the defect trails are too close together. This can compromise the cut-off point of the membrane microfilter and is only ameliorated by reducing overall porosity (which itself becomes a limitation). If the polymer material used is particularly thick or the etching process is not carefully controlled, the pores produced can take on a tapered character so that they are not square to the membrane surface. In addition, if the particle beam is not well-collimated, the angle of entry of the particles can vary widely with serious consequences for the quality of the microfilter formed. With all of these compromises and limitations, it is not surprising that track-etch membrane microfilters often fail to follow their theoretical models of performance.

The restrictions inherent in the manufacturing of track-etch membrane microfilters will often translate into application problems for the designer or engineer. For example, the track-etch membrane is manufactured in a separate process and must eventually be mated to some support structure in order to be used. Affixing the track-etch membrane to this support will necessitate the use of glues or thermo-welding process. Placing the membrane on the support structure is not trivial, nor is maintaining a taut, uniformly-stressed surface. Finally, the microfilter's composition may be incompatible with the intended use of the completed part.

A solution to these problems is found in a three-step manufacturing

process involving the creation of a moulded part, the embossing of that part, and the etching of the embossed region for a controlled breakthrough to create an *in situ* membrane microfilter on the part.

According to the invention, there is provided a method for manufacturing a membrane microfilter, comprising forming a blank having a web portion defining a filter region, embossing one side of the web portion in the filter region with an array of indentations of cross-sections comparable to a desired pore size of the filter, and ablating material from the web portion in the filter region until the indentation forms through pores of the desired pore size.

SHORT DESCRIPTION OF THE DRAWINGS

Figures 1a, 1b, and 1c show stages in the production of a blank for application of the method of the invention; all views in this and subsequent figures are cross-sectioned unless otherwise stated;

Figures 2a, 2b and 2c show successive stages in the embossing of the moulded blank;

Figure 3 shows an embossing tool;

Figure 4 shows deformation occurring when an embossing tool breaks through the blank;

Figures 5a and 5b show the result of misalignment of a two-part embossing tool;

Figure 6 shows damage to the embossing tool caused by it contacting a hard surface;

Figures 7a and 7b illustrate a method of operating the embossing tool;

Figures 8a and 8b show etching of the blank from the side opposite the tool;

Figures 9a and 9b show how pore characteristics can be controlled during the etching;

Figures 10a, 10b and 10c illustrate how different pore size may be formed

in the same blank, Figure 10c being a plan view.

Figure 1 illustrates the formation of a blank to be subsequently provided with an integral microfilter.

The precise technique used to create the moulded blank is not important to the invention. The blank may be pressure moulded from a starting blank c between two mould parts (as in Figure 1A), together defining a mould cavity d (see Figure 1B), or may be injection moulded, cast, or manufactured by any other applicable technique. What is important is that the blank has a defined filter region e in which the process membrane microfilter is required. It is usually advisable that this region be relatively thin compared to the rest of the blank, but it should be understood that the final thickness of the filter is determined by subsequent steps of the process. In practice, a thickness much less than 100 microns may be difficult to produce.

In the next step, the filter region c, where the membrane microfilter is required, is embossed (see figure 2), using an embossing tool E having an array of projections g so as to produce an array of indentations in one side of the filter region. The embossing technique is not critical. The embossing may be performed immediately after the blank is moulded while the material is still relatively soft. Alternatively, the embossing may take place as the part is moulded or may be a completely separate step. In any case, the region that requires the microfilter is embossed using a tool having an array of asperities g that can create an array of micro-indentations h in the molded part. The indentations may typically have a diameter up to 10 microns and a separation of at least 10 microns. Embossing tools f whose details include extremely high asperities (see Figure 3) can be easily manufactured by techniques such as microlithography. The drawback to this, or indeed any other embossing tool with such an array of micro-formed features is that the tool must be brought to bear against a hard surface n if the intention is to complete the microfilter formation in

this step. If the embossing tool simply breaks through the part to form the microfilter pores, the microfilter itself will be of poor quality, with a deformed surface as seen at k in Figure 4B, with a consequently wide distribution of pore sizes. If the embossing tool is designed to break through into a set of aligned wells m, there is a problem in obtaining precise alignment of the asperities with the wells to avoid tool damage (see Figures 5a and 5b). In either case, the tool will rapidly wear out if it is brought to bear against a hard surface during embossing - its delicate microstructure will be destroyed (see figure 6). Instead, the embossing tool is only used to create an array of precisely formed indentations in the microfilter region e of the blank (see Figure 7). It does not "break through" and so is not brought to bear against any other hard surface, greatly increasing tool life and preserving its microstructure.

In the final step in this procedure, the moulded, embossed part e is subjected to an *in situ* ablation procedure in the region of the embossing (see Figure 8). The ablation procedure may be any one of a range currently available, such as laser ablation, chemical etching, mechanical abrasion, or any other technique that may remove material from a surface in a specified region in a controlled manner. Material may be removed from the side of the region opposite the embossing, or from both sides.

As the material is removed from the embossed region, the embossed indentations will reach the opposite surface of the region, forming through pores p in the microfilter region of the blank so that it forms a membrane microfilter. An additional advantage of this technique is that the pore size may be controlled through the etching without comprising porosity or incurring overlap problems. For example, if the embossing tool has a microstructure consisting of an array of high-asperity cones then the embossed region will consist of an array of deep, conical wells. By removing a specified amount of material during the etching process, a pre-determined cone cross-section is revealed. If the etching is increased, the exposed cross-section is increased and the effective pore size s

rises uniformly (see Figure 9).

There is no inherent restriction on the material used in this three-step procedure. So long as the material can be molded, embossed, and etched in a controlled fashion, any substance may be used. A presently preferred material is polypropylene, although polystyrene is also advantageous. Furthermore, since the microfilter can be "post-processed" into the filter region of the moulded, embossed part, it is possible to stock-pile an enormous number of blanks for "just-in-time" microfilter manufacture that would correspond to a consumer's requirements. In de-coupling the microfilter blank manufacture from actual microfilter production, both may be separately optimized. This technique then allows the two to be varied independently without compromising the flexibility in pore dimensions often required by a range of customers.

The filter region of the blank can be moulded with a minimum thickness of about 100 microns, this being limited by the technique used to form the region, while the area of this region may be as large as required but is typically of the order of one square centimetre or less.

Any of a number of techniques may be used to produce the surface structure of the embossing tool. The fine structure of that embossing surface depends, to some extent, on the technique used to create it.

A presently preferred method for the manufacture of the embossing tool is the LIGA process (X-ray Lithographic, Galvanoformung, Abformtechnik (reference: E.W. Becker et al, *Microelectronic Engineering* 4, 35-56, 1986). In the LIGA process, a fine structure can be produced using an X-ray source in a photoresist material. Subsequent development of this resist creates a relief reproduction of the fine structure, although the resist itself is too fragile to be used directly. Electro-deposition fills the resist's surface with metal and when the resist is removed, the metal part is ready for use.

A typical embossing tool might have protuberances 10 microns in diameter, spaced by 20 microns. The protuberances themselves may be

tapered, as in Figures 7a and 7b, or cylindrical as in Figure 5A.

The depth of penetration of the hot embossing tool into the filter region depends on the thickness of the latter but is typically in the range of 10 to 100 microns.

A wide range of ablation techniques may be used, of which the following are only exemplary of subtractive micro-machining techniques that may be compatible with the invention having regard to the materials employed.

a. Wet chemical etching; in which a fluid etchant is introduced which dissolves away the plastic material. This is controlled by time of exposure and temperature. The exposure to the wet chemical is an isotropic process that will etch in all directions and so open out the pores (perhaps creating "craters"). So long as the process is predictable, this feature can be accommodated.

b. Cold photo-ablation; in which material is removed by the action of an ultraviolet laser capable of delivering direct bond-breaking energy to the work surface. This is highly directional and does not suffer from the isotropic action mentioned above.

c. Hot photo-ablation; in which material is removed by the action of a laser system (or other light source) that heats, melts and vapourizes the work material to remove it. Again, the action is directional, but the heat-damage effects can make this more difficult to control (a problem that does not appear in the cold-worked process above).

d. Laser machining with reactive gases; in which the laser is combined with a locally-present reactive gas such as chlorine (in the case of a silicon work material) that combines with the ablated material and carries it away. The result is a better definition of the surface features.

e. Focused ion beam milling; in which a mechanical drill bit is replaced by a focused column of energetic ions that are capable of cutting the material.

f. Ultrasonic etching in which an ultrasonic tool is set in motion and is coupled to the workpiece by an abrasive slurry. The mechanical motion of the ultrasonic tool drives the abrasive slurry to eat away at the workpiece.

g. Water jet machining; in which a high-velocity stream of water (with or without an abrasive) is used to cut the material in question.

h. Ultra-high precision mechanical machining; in which computer numerical controlled (CNC) milling machines capable of 0.05 micron steps are used to remove work material using single crystal diamond tools.

The quality of the finished filter of the invention should normally be greatly superior to its track-etched counterpart. Pore size can now be controlled to within a narrow tolerance and its statistical distribution is many times narrower than a comparable track-etched membrane. The use of an embossing tool to create the pore distribution over the microfilter's surface means that pore distributing can be precisely controlled. Thus, the porosity can be specified to within narrow tolerances depending on the requirements of the application. There is no danger of pore overlap and thus nothing to compromise the integrity of the filter cut-off.

In addition, the embossing tool may be produced with any desired array of cones, which need not all be of the same size (see Figure 10). After the post-processing etching, these can yield a variety in the size of pores within the filter in any desired arrangement.

A great advantage of the process of the invention is that the membrane microfilter can be included in a moulded part without the drawbacks encountered

in mechanical mounting methods. This reduces part cost, reduces manufacture time, and eliminates the problem of contamination during the mounting procedure.

CLAIMS

1. A method for manufacturing a membrane microfilter, comprising forming a blank having a web portion defining a filter region, embossing one side of the web portion in the filter region with an array of indentations of cross-sections comparable to a desired pore size of the filter, and ablating material from the web portion in the filter region until the indentation forms through pores of the desired pore size.

2. A method according to claim 1 wherein the web is embossed by a tool carrying an array of asperities of cross-section comparable to a desired pore size of the filter.

3. A method according to claim 2, wherein the asperities are tapered.

4. A method according to claim 2, wherein the asperities are cylindrical.

5. A method according to claim 2, 3 or 4, wherein the tool has asperities of more than one cross-section, such as to provide pores of more than one size.

6. A method according to any one of claims 1-5, wherein the web portion is ablated from its side opposite the side that is embossed.

7. A method according to any one of claims 1-6, wherein the web portion is ablated by chemical etching.

8. A method according to any one of claims 1-6, wherein the web portion is ablated by laser ablation.

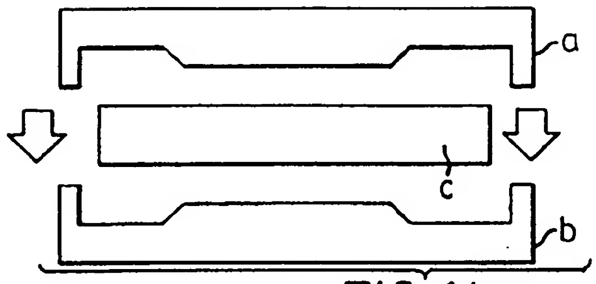


FIG. 1A

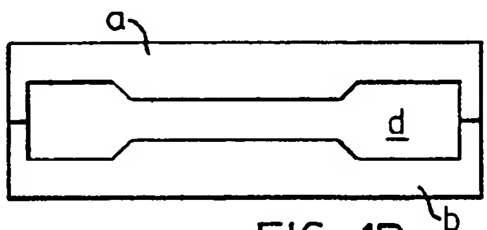


FIG. 1B

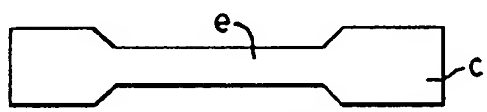


FIG. 1C

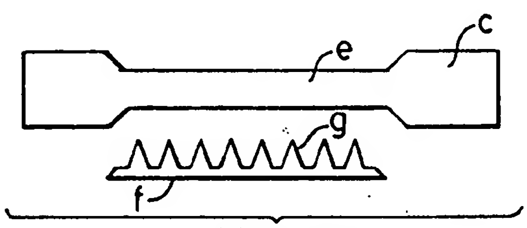


FIG. 2A

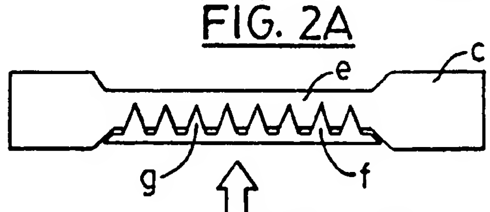


FIG. 2B

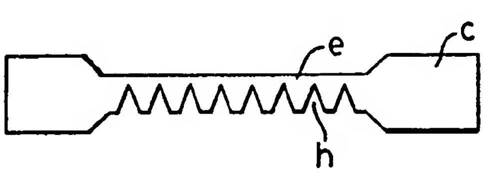


FIG. 2C

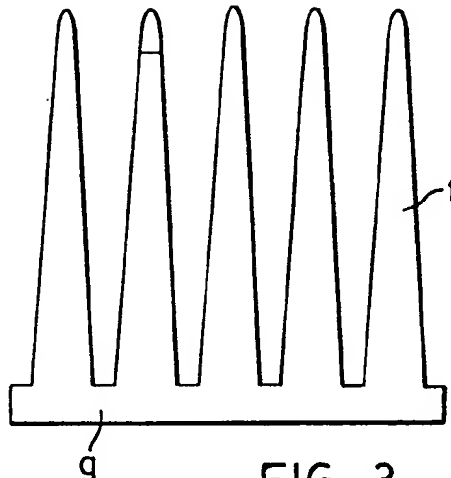


FIG. 3

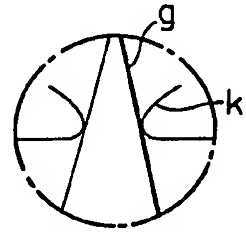


FIG. 4B

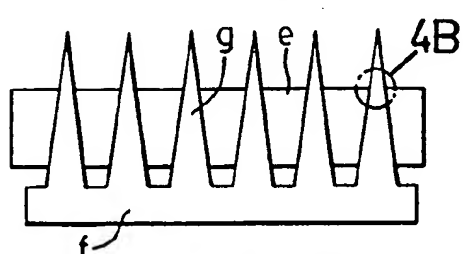


FIG. 4A

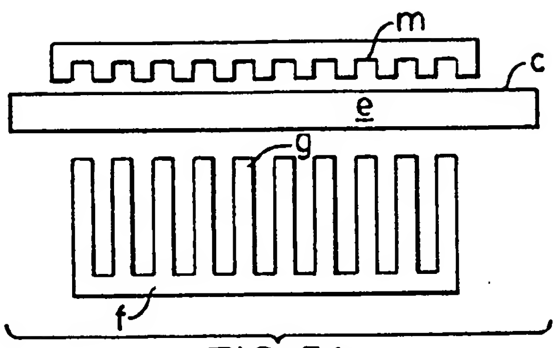


FIG. 5A

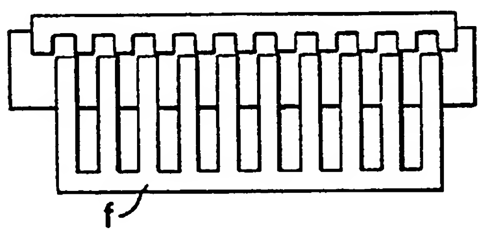


FIG. 5B

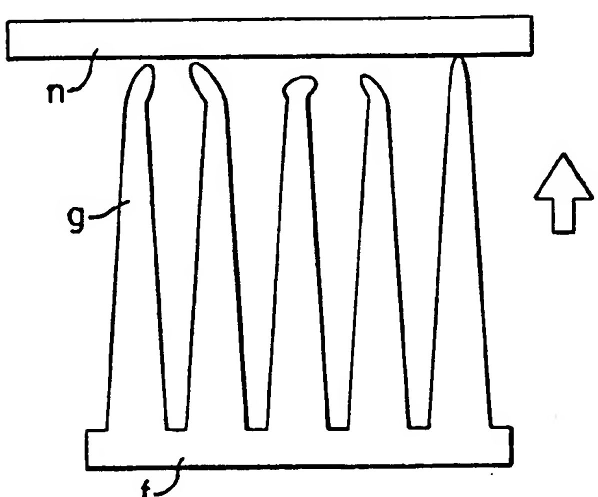


FIG. 6

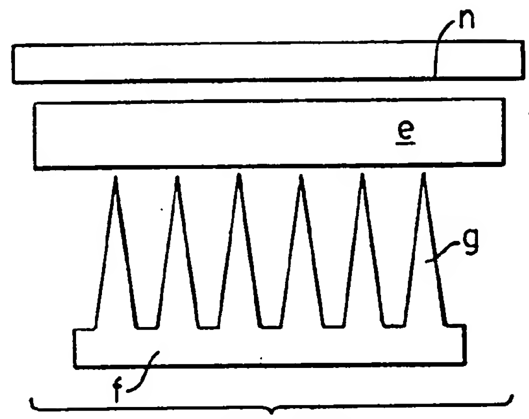


FIG. 7A

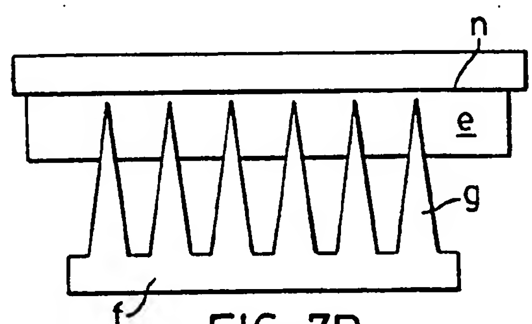


FIG. 7B

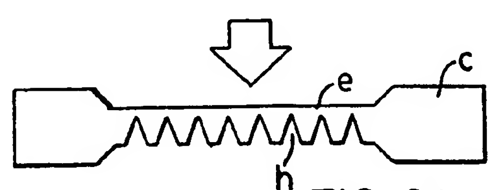


FIG. 8A

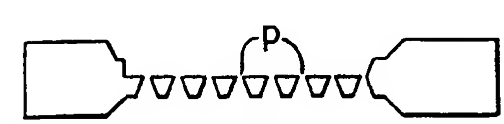


FIG. 8B

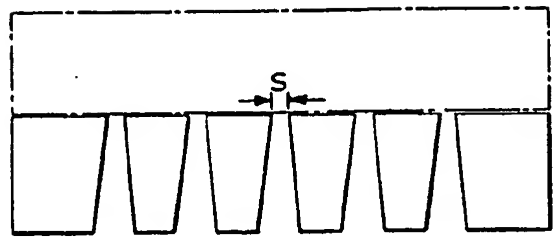


FIG. 9A

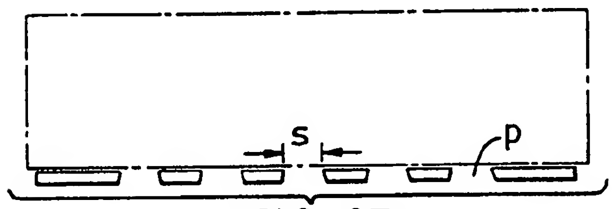


FIG. 9B

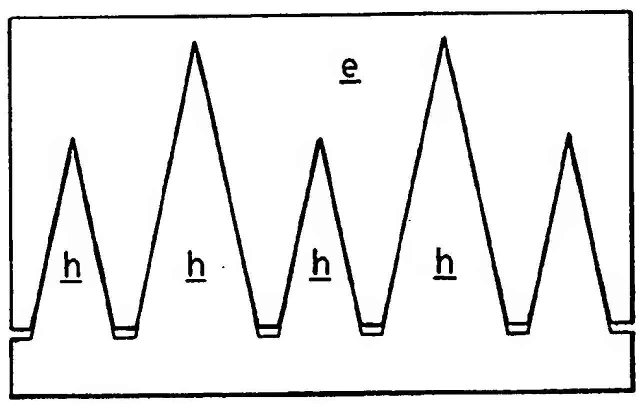


FIG. 10A

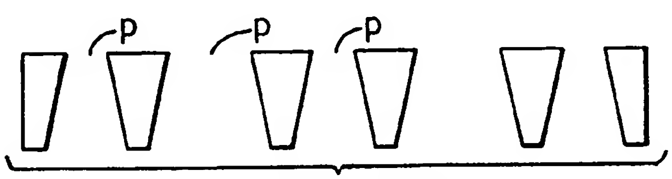


FIG. 10B

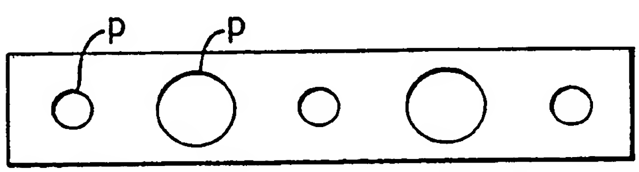


FIG. 10C

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 99/01242

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D67/00 B01D39/16 B26F1/24 B29C59/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01D B26F B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 317 399 A (COMMISSARIAT ENERGIE ATOMIQUE ;CENTRE NAT RECH SCIENT (FR)) 24 May 1989 (1989-05-24) page 3, line 12 - line 54; figures 1-5 ---	1,6,7
X	US 4 964 992 A (GOLDSMITH SUSAN H ET AL) 23 October 1990 (1990-10-23) column 5, line 22 -column 6, line 50 column 8, line 1 - line 22; figures 1-5 ---	1-4,7
X	US 3 929 135 A (THOMPSON HUGH ANSLEY) 30 December 1975 (1975-12-30) column 5, line 51 -column 6, line 10; figure 3 --- -/--	1-3,6

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 March 2000	24/03/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Eijkenboom, A

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Form PCT/ISA/210 (second sheet) (July 1992)

International Application No
PCT/CA 99/01242

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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1

INTERNATIONAL SEARCH REPORT

Information on patent family members

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